Preparation of Guanidinium Terminus-Molecularly Imprinted Polymers for Selective Recognition and Solid-Phase Extraction (SPE) Of [Arginine]-Microcystins

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Abstract

About 70 % of microcystin (MC) congeners reported in literature consist of L-arginine amino acid (R) with its guanidinium terminal extending out of the cyclic moiety of these MCs. Molecularly imprinted polymer (MIP) bearing guanidinium terminus cavities was successfully synthesised using L-arginine as a template. Non-imprinted polymer (NIP; without template) was also synthesised for control purposes. The surface area, total pore volume and average pore diameter of MIP and NIP were 267.13 m(2)/g, 0.63 cm(3)/g and 88.39 Å; 249.39 m(2)/g; 0.54 cm(3)/g and 87.14 Å, respectively. The polymers were investigated for selective recognition and extraction of [arginine]-MCs in water using solid-phase extraction/liquid chromatography-electrospray ionisation-mass spectrometry (SPE/LC-ESI-MS) method. Representative model standard solutions (0.5-10.0 μg/L) of MC-LR and MC-LY were spiked in distilled water, recovered by SPE and quantified by LC-ESI-MS. In this study, Oasis Waters™ HLB cartridges served as positive control SPE sorbents. The MIP recognised MC-LR with high recoveries (70.8-91.4 %; r(2) = 0.9962) comparable to HLB cartridges (71.0-91.85 %; r(2) = 0.9993), whereas the NIP did not recognise or retain MC-LR. Also, neither MIP nor NIP recognised or retained MC-LY. Extracts of environmental toxic Microcystis aeruginosa were subjected to SPE procedure employing MIP, NIP and HLB cartridges. Microcystin-LR, -YR, -RR, -WR, -(H4)YR and (D-Asp(3), Dha(7))MC-RR were extracted by MIP and HLB cartridges only as confirmed by LC-ESI-MS. This study demonstrated that the prepared MIP have potential applications for the removal in water and LC-ESI-MS identifications of MCs consisting the guanidinium moiety, i.e.[arginine]-MCs, and in particular targeting commonly encountered toxic congeners, MC-LR, -YR and -RR.

Keywords

Guanidinium terminus
MIP
SPE
Selective recognition
[arginine]-Microcystins